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(54) Title: HERBICIDAL COMPOSITIONS

(57) Abstract: Amido alkyl amine oxides, optionally blended with ether carboxylates, amphoteric surfactants, chelants, solvents, hydrotropes and/or wetting agents are used to prepare glyphosate solution concentrates.

HERBICIDAL COMPOSITIONS

The present invention relates to concentrated herbicidal compositions comprising water soluble glyphosate salts and a surfactant.

A number of formulations have been proposed whereby the herbicide N-(phosphonomethyl)glycine, alias glyphosate, may be supplied as a concentrated aqueous solution with a surfactant synergist which aids wetting and penetration, when the composition is diluted with water and applied to herbage.

The surfactants which have so far proved most cost effective for these purposes have been ethoxylated amines. The latter however have a poor environmental profile being biotoxic and poorly biodegradable. There is a demand for a more environmentally acceptable alternative to amine ethoxylates.

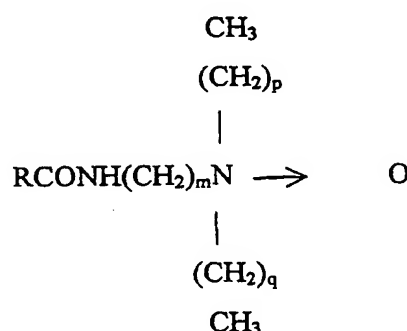
Factors governing the choice of surfactant include wetting power, herbicidal or synergistic action, environmental profile and ability to form stable solutions with glyphosate at as high a concentration as possible, as well as cost. A particularly important factor is low foaming. Most surfactants cause undesirable foam levels. These not only make handling more difficult but also impair biocidal effectiveness.

The use of trihydrocarbyl amine oxides has been proposed in WO 97/36491. However these have been found to give undesirably viscous compositions at economically desirable concentrations.

We have discovered that ether carboxylates meet most of the above criteria and in particular give enhanced biocidal action but are insufficiently soluble in concentrated glyphosate solutions. We have found (see WO/00/38523) that betaines can solubilise ether carboxylates, but that high salt levels normally associated with betaines tend to precipitate glyphosate. Desalted betaines are available but are expensive. We have now discovered that certain alkyl amido amine oxides also meet most of the above criteria and in addition are soluble and can act as cosurfactants, solubilising ether

carboxylates. The trihydrocarbyl amine oxides are not readily compatible with ether carboxylates.

The invention provides a herbicidal solution concentrate comprising from 30% by weight, to saturation of a water soluble glyphosate salt and from 8 to 20% by weight of surfactant comprising: 10 to 100% by weight based on the total weight of surfactant of an alkyl and/or alkenyl amido amine oxide of the formula:



where R is a C₆₋₂₀ alkyl or alkenyl group, m is 1 to 4, and p and q are independently 0 to 3; and from 0 to 90% by weight based on the total weight of surfactant of ether carboxylate.

The glyphosate is preferably present as its potassium, ammonium, C₂ to 3 amine or mono or di ethanolamine salt, or as a mixture of two or more of said salts. Particularly preferred is the isopropylamine salt.

We prefer that (m + the number of carbon atoms in R) is from 7 to 19 and that p and q are each 0. We particularly prefer that m is 2 or most preferably 3. R is desirably 8 or 10. Amine oxides in which the majority of the amido alkyl groups are of the same length are particularly preferred. Especially preferred are N-octanoamidopropyl-N, N-dimethyl amine oxide, and N-decanoamidopropyl-N, N-dimethyl amine oxide. The amine oxide may optionally be derived from a coconut or palm fatty acid, especially one which has been "topped", i.e. has had the higher mol weight constituents such as C₁₄+, removed or reduced.

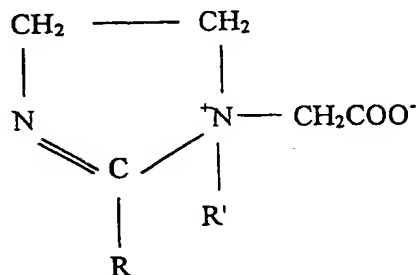
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We prefer that the amine oxide should constitute at least 20 and preferably more than 30% by weight of the total surfactant especially 40 to 80%.

The presence of an ether carboxylate is preferred, since it provides enhanced biocidal activity. The ether carboxylate preferably constitutes at least 10% , more preferably greater than 20, especially more than 30% of the total weight of surfactant.

The ether carboxylate is an alkyl alkenyl or alkaryl poly alkoxy carboxylate such as $RO[(CH_2)_nO]_mCH_2CO_2^-$ where R is an alkyl, alkenyl or alkaryl phenyl group having from 8 to 20 aliphatic carbon atoms, each n is 2 to 4, preferably 2 and m is 1 to 30, preferably 2 to 20, e.g. 3 to 10. The counter ion may comprise sodium but is preferably potassium or ammonium or an amine e.g. a C_2 to C_3 amine or an alkanolamine. We particularly prefer narrow cut C_8 and C_{10} alkyl polyethoxy carboxylates.

The surfactant may additionally comprise an amphoteric surfactant. The amphoteric surfactant may for example be a betaine, e.g. a betaine of the formula: $R_3N^+CH_2COO^-$, wherein each R is an alkyl, cycloalkyl, alkenyl or alkaryl group and preferably at least one, and most preferably not more than one R, has an average of from 6 to 14, e.g. 8 to 10 aliphatic carbon atoms and each other R has an average of from 1 to 4 carbon atoms. It may also comprise a so called "imidazoline" betaine traditionally ascribed the formula:



wherein R and R' are alkyl, alkenyl, cycloalkyl, alkaryl or alkanol groups having an average of from 1 to 20 aliphatic carbon atoms and R preferably has an average of

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from 6 to 20, e.g. 8 to 14 aliphatic carbon atoms and R' preferably has 1 to 4 carbon atoms. In practise "imidazoline" betaines are normally present substantially entirely as the non-cyclic N-amido-alkyl betaine. Other amphoteric surfactants for use according to our invention include alkyl amino polyalkoxy sulphates, sulphobetaines and other quaternary amine or quaternised imidazoline sulphonic acids and their salts, and Zwitterionic surfactants, e.g. N-alkyl taurines, carboxylated amido amines such as $RCONH(CH_2)_nN^+R'_2CH_2CO_2^-$ where n is 2 to 4, and amino acids having, in each case, hydrocarbon groups capable of conferring surfactant properties (e.g. alkyl, cycloalkyl alkenyl or alkaryl groups having from 8 to 20 aliphatic carbon atoms). Typical examples include 2-tallow alkyl, 1-tallow amido alkyl, 1-carboxymethyl imidazoline, 2-coconut alkyl N-carboxymethyl 2 (hydroxyalkyl) imidazoline, coconut amido propyl dimethyl betaine and C₁₂₋₁₄ alkyl dimethyl betaine. Generally speaking any water soluble amphoteric or Zwitterionic surfactant compound which comprises a hydrophobic portion including C₈₋₂₀ alkyl or alkenyl group and a hydrophilic portion containing an amine or quaternary ammonium group and a carboxylate, sulphate or sulphonic acid group may be used in our invention.

The amphoteric surfactant may constitute from 0 to 90% more usually less than 90%, preferably less than 70%, especially less than 50% by weight of the total surfactant.

It is strongly preferred when an amphoteric surfactant is selected to use a low sodium version, to avoid precipitation of sodium glyphosphate. Typically the concentration of sodium ion in the composition should be less than 0.035% based on the total weight of the composition.

We prefer that the surfactant consist essentially of the amine oxide, ether carboxylate and, optionally, the amphoteric surfactant. We do not, however, exclude the presence of minor amounts, e.g. up to 15%, preferably less than 10% by weight of the total surfactant, of other surfactants such as non-ionic surfactants including alkylethoxylates and alkanolamides and anionic surfactants such as alkyl ether sulphates, alkyl sulphates, alkyl benzene sulphonates and soaps. In particular it is often advantageous to include up to 15% by weight of a wetting agent.

The formulation may conveniently contain chelating or sequestering agents to enhance the performance of the product in hard water. For example calcium and/or magnesium sequestrants, such as phosphates, polyphosphates, polycarboxylates, amino carboxylates, phosphonates and, in particular, amino phosphonates, may be present in effective amounts. Specific examples include potassium pyrophosphate, sodium tripolyphosphate, ammonium hexametaphosphate, citric acid, polyacrylic acid, nitrilotriacetic acid, ethylene diamine tetracetic acid, acetodiphosphonic acid, amino tris (methylenephosphonic) acid, ethylene diamine tetrakis (methylene phosphonic) acid and especially diethylene triamine pentakis (methylene phosphonic) acid.

The chelant may be present in the acid form or as a water soluble salt, however for reasons stated above we prefer that the amount of sodium be limited: We therefore prefer that the chelant if present as a salt be present as the potassium or more preferably ammonium salt or as an amine or alkalolamine salt. The chelant is preferably present in concentrations of from 0.05 to 5% especially 0.1 to 1% e.g. 0.2 to 0.5%.

The solution concentrate does not normally require the presence of solvents, however they can be tolerated and may be adventitiously present as constituents of surfactant blends used to prepare the solution concentrates.

We generally prefer to supply surfactants for use in the preparation of the solution concentrates in the form of concentrated blends. The latter may require small amounts of solvent for stability. Typically the blends contain: from 10 to 70% more preferably 20 to 60% e.g. 30 to 50% ether carboxylate by weight of the blend; from 20 to 80% more preferably 30 to 70% e.g. 40 to 60% of the amidoalkyl amine oxide by weight of the blend; and from 3 to 50% more preferably 5 to 40% e.g. 10 to 30%, by weight of the blend, of solvent.

The solvent is typically a water miscible mono, di- or polyhydric alcohol or glycol ether such as ethanol, isopropanol, ethylene glycol, glycerol, ethylene glycol

monomethyl ether, diethylene glycol monomethyl ether or preferably polyethylene glycol. We prefer a polyethylene glycol with a mean molecular weight of from 90 to 300, e.g. 130 to 250.

The surfactant blend may optionally contain minor amounts of hydrotrope such as a C₁ to 5 alkyl benzene sulphonate e.g. a potassium, ammonium or amine xylene sulphonate, if required to inhibit gelling. We prefer to use the minimum amount required to achieve the desired effect which will usually be between 0.1 and 5% of the weight of the blend.

The invention provides the use of blends of ether carboxylate and amidoalkyl amine oxide to prepare glyphosate solution concentrates and to such blends for use in preparing the concentrates and to sprayable solutions prepared by diluting the solution concentrate with water.

We prefer that the pH of the solution concentrate be adjusted to from 3 to 7 preferably 4 to 6 e.g. 4.5 to 5.5 with a base that does not precipitate glyphosate, such as ammonia or an amine.

The invention will be illustrated by the following examples in which the glyphosate was used as the isopropylamine salt and weights of glyphosate are all quoted as gm acid equivalent per litre solution. Surfactants and glycol are all quoted as g. active matter per litre of solution.

"EMPICOL" is a Registered Trade Mark of Albright & Wilson UK Limited

CVE is C₈ alkyl 5 mole ethoxy carboxylate

CVH is C₈ alkyl 8 mole ethoxy carboxylate

"C₈ amido amine oxide" is N-octanoamidopropyl-N,Ndimethylamine oxide

"C₁₀ amido amine oxide" is N-decanoamidopropyl-N,Ndimethylamine oxide

Example 1

Glyphosate	360
C ₈ amidoamine oxide	75
"EMPICOL" CVE	75
PEG 200	40
Water	to 1l
Ammonia solution	to pH 5

Example 2

Glyphosate	360
C ₈ amidoamine oxide	50
"EMPICOL" CVE	100
PEG 200	40
Water	to 1l
Ammonia solution	to pH 5

Example 3

Glyphosate	360
C ₈ amidoamine oxide	43
"EMPICOL" CVE	107
Water	to 1l
Ammonia solution	to pH 5

Example 4

Glyphosate	360
C ₈ amidoamine oxide	35.7
"EMPICOL" CVE	89.3
Water	to 1l
Ammonia solution	to pH 5

Example 5

Glyphosate	360
C ₈ amidoamine oxide	75
"EMPICOL" CVH	75
PEG200	40
Water	to 1l
Ammonia solution	to pH 5

Example 6

Glyphosate	360
C ₁₀ amidoamine oxide	75
"EMPICOL" CVE	75
PEG 200	40
Water	to 1l
Ammonia solution	to pH 5

Example 7

Glyphosate	360
C ₁₀ amidoamine oxide	50
"EMPICOL" CVE	100
PEG 200	40
Water	to 1l
Ammonia solution	to pH 5

Example 8

Glyphosate	360
C ₁₀ amidoamine oxide	75
"EMPICOL" CVH	75
PEG200	40
Water	to 1l
Ammonia solution	to pH 5

Example 9

Glyphosate	360
"EMPICOL" CVH	100
C ₁₀ amidoamine oxide	50
"BRIQUEST" 301-50A	5.5
PEG200	40
Water	to 1L
Ammonia solution	to pH 5

Example 10

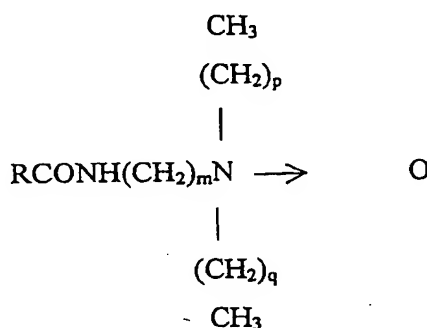
Glyphosate	360
"EMPICOL" CVH	69.1
C ₁₀ amidoamine oxide	50
"EMPILAN" KI 6.5	5.5
PEG200	40
Water	to 1L
Ammonia solution	to pH 5

Each of the above formulations was a clear, stable solution which gave very low foam in comparison to the standard commercial product. In each case the formulation was prepared from a blend of the ether carboxylate (which is supplied as 85% aqueous solution) amine oxide (as 40% aqueous solution) and any solvent, chelant or wetting agent.

The blends were stable and dispersed easily in water together with the glyphosate. The pH of the formulation was finally adjusted with ammonia.

CLAIMS

1. A herbicidal solution concentrate comprising from 30% by weight, to saturation of a water soluble glyphosate salt and from 8 to 20% by weight of surfactant comprising: 10 to 100% by weight based on the total weight of surfactant of an alkyl and/or alkenyl amido amine oxide of the formula:



where R is a C₆₋₂₀ alkyl or alkenyl group, m is 1 to 4, and p and q are independently 0 to 3; and from 0 to 90% by weight based on the total weight of surfactant of ether carboxylate.

2. A solution according to claim 1 wherein the glyphosate is present as its ammonium, C₂ to 3 amine, alkanolamine or methosulphate salt.
3. A solution according to either of claims 1 and 2 which additionally comprises an amphoteric surfactant.
4. A solution according to any foregoing claim comprising up to 15% by weight of a wetting agent.
5. A solution according to any foregoing claim comprising a up to 5% by weight of a chelant.

6. A solution according to claim 5 wherein the chelant is an amino phosphonate.
7. A solution according to any foregoing claim having a pH between 4.5 and 5.5.
8. A composition according to any foregoing claim containing at least 10% of an ether carboxylate which is a compound of the formula $RO[CH_2CH_2O]_mCH_2CO_2M$ where R is an alkyl, alkenyl or alkylphenol group having from 6 to 20 aliphatic carbon atoms m is 1 to 30 and M is potassium, ammonium or an amine.
9. The use of a blend of surfactants comprising an alkyl ether carboxylate and amido alkyl amine oxide to prepare a glyphosate solution concentrate.
10. An aqueous blend of surfactants for use according to claim 9 comprising, by weight of the blend, 10 to 70% ether carboxylate, 20 to 80% amidoalkyl amine oxide and 5 to 40% by weight of a water miscible mono-di- or polyhydroxy alcohol or alcohol ether.
11. A herbicidal spray prepared by diluting a solution concentrate according to any of claims 1 to 8 with water.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 00/02865

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A01N25/30 A01N57/20 C11D1/75 C11D1/06 C11D1/86		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A01N C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 36491 A (ALBEMARLE CORP) 9 October 1997 (1997-10-09) cited in the application page 3, line 3-18; tables 1-3,7 -----	1-11
P,A	WO 00 38523 A (MILLE FABIEN HERVE JOSEPH ; OXFORD PHILIP JAMES (GB); ALBRIGHT & WI) 6 July 2000 (2000-07-06) cited in the application page 1, paragraph 5 -page 3, paragraph 1 -----	1-11
A	EP 0 508 667 A (WITCO CORP) 14 October 1992 (1992-10-14) page 3, line 1-29; examples 10-13 -----	1-11
A	EP 0 560 570 A (AMWAY CORP) 15 September 1993 (1993-09-15) page 3, line 31-43; claims 1,2,6-8,12 -----	10
<div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*G* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">3 November 2000</div>		Date of mailing of the international search report <div style="text-align: center;">10/11/2000</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center;">Klaver, J</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/02865

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9736491	A	09-10-1997	US 5700760 A	23-12-1997
			CA 2250340 A	09-10-1997
			DE 69700789 D	16-12-1999
			DE 69700789 T	15-06-2000
			EP 0902622 A	24-03-1999
WO 0038523	A	06-07-2000	AU 2284900 A	31-07-2000
EP 0508667	A	14-10-1992	US 5118444 A	02-06-1992
			AT 138782 T	15-06-1996
			AU 644954 B	23-12-1993
			AU 1472992 A	15-10-1992
			BR 9201280 A	01-12-1992
			CA 2065193 A	11-10-1992
			DE 69211208 D	11-07-1996
			DE 69211208 T	28-11-1996
			DK 508667 T	19-08-1996
			ES 2090504 T	16-10-1996
			GR 3020947 T	31-12-1996
			JP 5112403 A	07-05-1993
			MX 9201640 A	01-10-1992
			NZ 242087 A	25-02-1994
EP 0560570	A	15-09-1993	US 5298195 A	29-03-1994
			AU 3029392 A	16-09-1993
			CA 2085036 A	10-09-1993
			EP 0854181 A	22-07-1998
			JP 6009988 A	18-01-1994
			US 5443757 A	22-08-1995